987. *The Chemistry of Fungi. Part XXIX.*[1] *The Degradation of Di- and Tetra-hydrosclerotiorin with Alkali.*

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The degradation of tetrahydrosclerotiorin with alkali affords hydrochloric acid, formic acid, traces of 4 : 6-dimethyl-*n*-octanoic acid, and a dihydroxynaphtha-*p*-quinone (tetrahydrosclerotoquinone), $C_{19}H_{22}O_2(OH)_2$. The genesis, degradation, and structure of this quinone are discussed and possible formulæ deduced. Dihydrosclerotiorin undergoes an analogous series of transformations.

On degradation with alkali sclerotiorin (I) gives formic, hydrochloric, and 4 : 6-dimethylocta-2 : 4-dienoic acid as the only characterisable fragments.[1] Under similar conditions tetrahydrosclerotiorin furnishes, in addition to formic, hydrochloric, and negligible amounts of the expected 4 : 6-dimethyl-*n*-octanoic acid, a product, named tetrahydrosclerotoquinone, $C_{19}H_{22}O_2(OH)_2$. This is shown to be a dihydroxynaphtha-*p*-quinone, forming a di-*O*-methyl ether, $C_{19}H_{22}O_2(OMe)_2$, and a di-*O*-acetate, $C_{19}H_{22}O_2(OAc)_2$, and on general grounds and in keeping with the molecular rotation is held to retain the saturated side-chain present in the parent compound. The remarks[1] regarding the existence of pairs of diastereoisomerides from the mixture of α- and β-tetrahydrosclerotiorin, m. p. 142—144°, apply to this quinone. In the present instance a second isomeride has not been detected. Reductive acetylation of tetrahydrosclerotoquinone gives tetra-*O*-acetyltetrahydrosclerotoquinol. Since the ultraviolet absorption of a chromophore is but little affected by substitution with acetoxyl groups,[2] a comparison of the ultraviolet

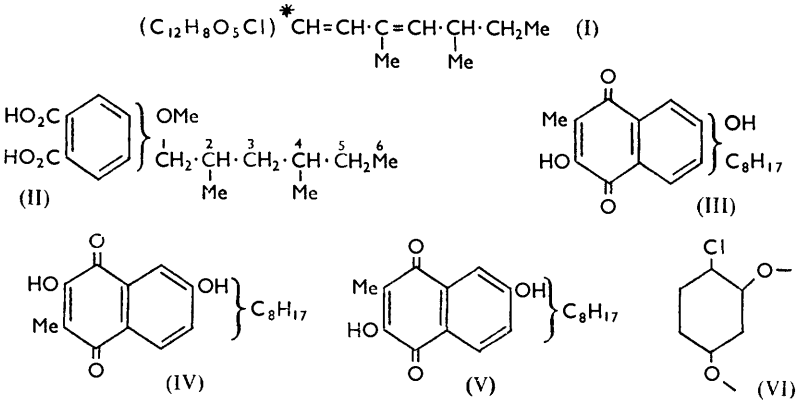
[1] Part XXVIII, Eade, Page, Robertson, Turner, and Whalley, preceding paper.
[2] Cooke, Macbeth, and Winzor, *J.*, 1939, 878.

absorption spectra of tetrahydro- and di-*O*-acetyltetrahydro-sclerotoquinone and tetra-*O*-acetyltetrahydrosclerotoquinol with those of 2-hydroxy-1 : 4-naphthaquinone, 1 : 4-naphthaquinone, and naphthalene respectively (cf. Table) indicates that tetrahydrosclerotoquinone is a naphthalene derivative. In addition, the spectral data clearly show that sclerotoquinone is a 1 : 4- and not a 1 : 2-quinone,[2] in agreement with the failure of tetrahydrodi-*O*-methylsclerotoquinone to form a quinoxaline derivative.

As expected, the main absorption peaks in the spectra of the acetates derived from tetrahydrosclerotoquinone and tetrahydrosclerotoquinol are shifted to wavelengths 10—15 mμ longer than those for the corresponding naphthalene, owing to the bathochromic effect of the alkyl substituents (see Table).

Compound	$\lambda_{max.}$ (mμ)	log ε	Compound	$\lambda_{max.}$ (mμ)	log ε
Tetrahydrosclerotoquinone	273	4·56	2-Hydroxy-1 : 4-naphtha-	244	4·20
	307	4·19	quinone [2]	276	4·20
	347	3·75		331	3·45
Di-*O*-acetyltetrahydroscleroto-	258	4·48	1 : 4-Naphthaquinone [2]	246	4·28
quinone	276	4·30		256	4·13
	342	3·58		334	3·44
Tetra-*O*-acetyltetrahydro-	234	4·94	Naphthalene [3]	220	5·05
sclerotoquinol	289	3·79		275	3·75
	336	1·89		314	2·50

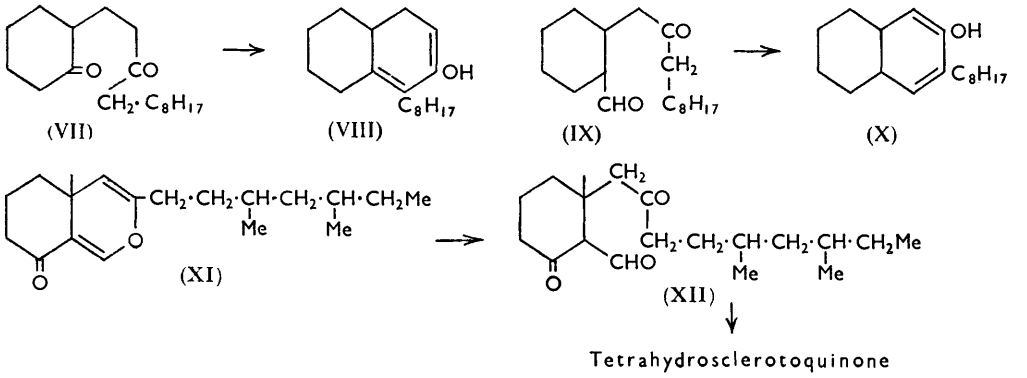
On oxidation with potassium permanganate tetrahydrodi-*O*-methylsclerotoquinone gave an optically active *x*-(2 : 4-dimethyl-*n*-hexyl)-*y*-methoxyphthalic acid (II) which forms an anhydride having infrared absorption at 1845 and 1721 cm.$^{-1}$ and readily yielding an anilic, a toluidic, and a β-naphthylamic acid. The composition of the methoxyphthalic acid and its derivatives shows that, in the oxidation of the *p*-quinonoid ring of tetrahydrodi-*O*-methylsclerotoquinone, a *C*-methyl and a methoxyl group have been removed and hence the quinone may be represented as (III). Since on demethylation the methoxyphthalic acid furnished a hydroxyphthalic acid which has a negative ferric reaction the hydroxyl group cannot be in the *o*-position to either of the carboxyl groups, and the formula for tetrahydrosclerotoquinone may be expanded to (IV) or (V). Further, from the composition of the methoxyphthalic acid and in agreement with its molecular rotation, the compound and hence sclerotoquinone and its dimethyl ether retain a C_8H_{17} residue from the saturated side-chain present in tetrahydrosclerotiorin.



From the failure of repeated attempts to prepare from sclerotiorin a quinone analogous to tetrahydrosclerotoquinone it appears reasonable to conclude that the presence of a

[3] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Ed. Arnold, London, 1954, p. 122.

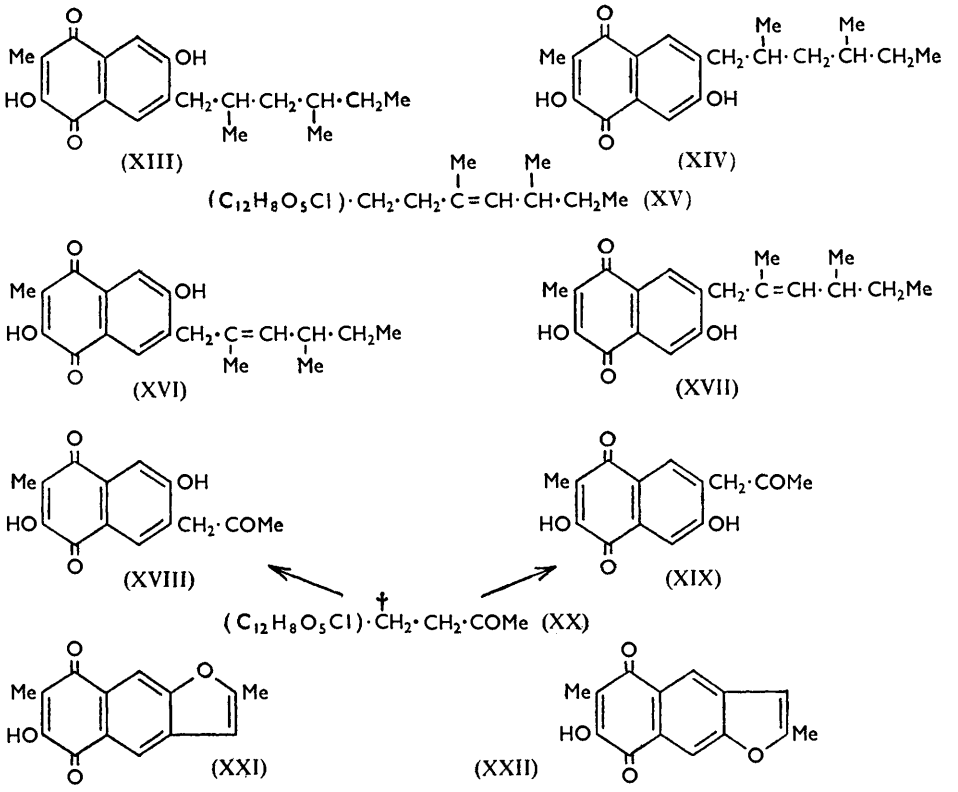
methylene group at the position marked * in the side-chain [see formula (I)] is essential for the formation of tetrahydrosclerotoquinone and that this compound is an artefact arising by a modification of the sclerotiorin kernel. Further, in the formation of the quinone the original side-chain C_9H_{19} of tetrahydrosclerotiorin has been shortened by a methylene group, which is involved in the formation of the benzene ring retaining the residual C_8H_{17} alkyl residue, exemplified in the cyclisation of (VII) to (VIII) or (IX) to (X).



From the methods of formation, the properties, and information available on the partial structure of sclerotinol [1] and of tetrahydrosclerotoquinone it seems reasonable to conclude that sclerotiorin contains a potentially aromatic ring system, aromatisation of which is invariably accompanied by simultaneous elimination of two carbon atoms or of a C_2 residue, leading to the benzene ring in sclerotinol and sclerotol [1] and to the quinonoid ring of tetrahydrosclerotoquinone. Further, the chlorine atom, which is attached to the aromatic ring of sclerotinol and sclerotol, is presumably contained in the parent hydroaromatic ring of sclerotiorin. Under the alkaline conditions obtaining during the transformation of tetrahydrosclerotiorin into tetrahydrosclerotoquinone the halogen atom is replaced by an oxygen system and it therefore seems likely that in the hydroaromatic unit of the sclerotiorin kernel the chlorine atom and the two oxygen atoms possess the relative arrangement (VI). From an inspection of the partial structures developed for sclerotinol and sclerotol in Part XXVIII [1] with the formula (IV) or (V) for tetrahydrosclerotoquinone it follows that the conclusions regarding the orientation of this quinone are compatible with the deductions concerning the orientation of sclerotinol and sclerotol and with their formation from the kind of structural unit [1] suggested to account for the production of sclerotioramine and its *N*-substituted products, *i.e.*, there is present the unit (XI) which can open to give (XII), or an enolic form of it, and this with ammonia or primary amines gives the amino-derivative (Part XXVIII) [1] and with alkali undergoes cyclisation to tetrahydrosclerotoquinone. This concept of the formation of the non-quinonoid ring of tetrahydrosclerotoquinone according to the scheme (IX) ⟶ (X) also rationalises, *inter alia*, the production of formic acid in the alkaline degradation of sclerotiorin and of tetrahydrosclerotiorin, the failure of sclerotiorin to produce a quinone analogous to tetrahydrosclerotoquinone, and the formation in high yield of 4 : 6-dimethylocta-2 : 4-dienoic acid from sclerotiorin in contrast with the negligible quantity of 4 : 6-dimethyl-*n*-octanoic acid obtained from tetrahydrosclerotiorin. The conclusions concerning tetrahydrosclerotoquinone and its degradation are also in agreement with the deduction, from the orientation of sclerotinol, that the C_{10} residue of sclerotiorin is separated from the aromatic ring of sclerotinol by one carbon atom present as a methylene group.[1] On these views it seems clear that the phenolic hydroxyl group retained as methoxyl in the phthalic acid residue, prepared from tetrahydrosclerotoquinone, is derived from the

oxygen which is present as the carbonyl group in the dienoic acid and consequently the structure of tetrahydrosclerotoquinone is reduced to one of the alternatives (XIII) or (XIV).

In confirmation of the hypothesis that a methylene group at position * of the side-chain (cf. I) in sclerotiorin derivatives is essential for the quinone formation, it has been found that degradation of dihydrosclerotiorin (XV) [1] by alkali leads to simultaneous elimination of two carbon atoms and formation of a dihydroxynaphtha-*p*-quinone (dihydrosclerotoquinone), $C_{19}H_{20}O_2(OH)_2$, which readily yields a di-*O*-methyl ether, a di-*O*-acetate, and, on reductive acetylation, tetra-*O*-acetyldihydrosclerotoquinol, $C_{19}H_{20}(OAc)_4$. Like tetrahydrosclerotoquinone, dihydrosclerotoquinone does not form a quinoxaline derivative,



and the ultraviolet absorption spectra of the quinone diacetate and quinol tetra-acetate indicate that the compound is a naphtha-*p*-quinone and hence may be formulated as (XVI) or (XVII).

Ozonolysis of tetra-*O*-acetyldihydrosclerotoquinol and subsequent deacetylation of the product followed by aerial oxidation gave an acetonyl-hydroxy-*p*-quinone, dihydropentanorsclerotoquinone (XVIII) or (XIX) whose partial orientation is confirmed by its conversion on sublimation into a coumarone, (XXI) or (XXII); this coumarone was originally isolated in the purification of the acetonyl-hydroxy-quinone. The quinone (XVIII) or (XIX) is also obtained by the alkaline degradation of the compound [1] (XX) in which the requisite methylene group involved in the naphthaquinone formation is present at the carbon atom marked † in formula (XX). The production of a coumarone derivative in this manner serves to substantiate the relative positions of the hydroxyl and acetonyl residue in the benzenoid ring of the naphthaquinone derived from dihydrosclerotiorin. From this

it follows that dihydrosclerotoquinone may be formulated as (XVI) or (XVII) and therefore tetrahydrosclerotoquinone is represented by (XIII) or (XIV).

With dihydrosclerotoquinone there was obtained from the compound (XX) a small amount of a chlorine-containing, non-quinonoid phenol, $C_{14}H_{13}O_4Cl$, the yield of which can be somewhat increased by lowering the temperature of alkaline degradation. Since it cannot be converted into dihydropentanorschlerotoquinone (XVIII or XIX) under the standard conditions this compound does not appear to be an intermediate in the quinone formation.

Experimental

Degradation of Tetrahydrosclerotiorin with Alkali.—(*a*) Tetrahydrosclerotiorin (2 g.), zinc dust (3 g.), and 5% aqueous potassium hydroxide (100 ml.) were heated under reflux in nitrogen for 5 min. and the effluent gases were passed into a solution of 2 : 4-dinitrophenylhydrazine sulphate to trap volatile carbonyl compounds; a precipitate was not formed. The cooled, filtered mixture was acidified and the precipitate and solution extracted with ether (4 × 20 ml). The combined extracts were washed successively with aqueous 2N-sodium hydrogen carbonate, 2N-sodium carbonate, and 2N-sodium hydroxide, and the washings were acidified. The sodium hydrogen carbonate extract did not give a precipitate and the caustic extract gave an intractable red gum. From the aqueous sodium carbonate washings there was obtained an orange-brown solid (1·4 g.) which was purified by sublimation at 200°/0·005 mm., followed by crystallisation from methanol, giving *tetrahydrosclerotoquinone* in orange plates (0·7 g.), with a port-wine ferric reaction in alcohol, $\lambda_{max.}$ 273, 310, 345 mμ (log ε 4·50, 4·24, 3·80 respectively), and m. p. 218° [Found: C, 72·1, 72·1, 72·1; H, 7·6, 7·7, 7·6; Cl, 0%; *M* (Rast), 329. $C_{19}H_{24}O_4$ requires C, 72·1; H, 7·7%; *M*, 316], $[\alpha]_D^{20}$ 6·6° (*c* 1·37 in EtOH), $[M]_D^{20}$ +2085°. This compound is readily soluble in the usual organic solvents except light petroleum (b. p. 60—80°), and in 2N-aqueous sodium hydroxide or 2N-aqueous sodium carbonate gives a purple solution. A rather smaller yield of the same product was obtained in the absence of zinc dust.

(*b*) To ensure the absence of traces of acetic acid retained from its purification tetrahydrosclerotiorin (10 g.), dissolved in ether (700 ml.), was washed successively with 2N-aqueous sodium hydrogen carbonate (6 × 50 ml.) and water (4 × 70 ml.), and recovered by drying and evaporation. Degradation of the compound in batches (2 g. each) was performed as described in (*a*). The combined alkaline solutions were filtered, acidified with sulphuric acid, again filtered, and distilled in a current of steam until the distillate was no longer acidic; the volume of solution being distilled was maintained by the addition of distilled water as required. The distillate contained chloride ions and was neutralised with 0·1N-sodium hydroxide and evaporated, leaving a residue of colourless sodium salts (1·5 g.). Interaction of this with *o*-phenylenediamine in the usual manner gave benziminazole (0·8 g.) in needles, m. p. and mixed m. p. 190° (mixed m. p. with 2-methylbenziminazole, *ca.* 132°). The picrate had m. p. and mixed m. p. 228° (admixed with 2-methylbenziminazole picrate, it had m. p. 180—186°).

The 2 : 4-*dinitrophenylhydrazone* of tetrahydrosclerotoquinone separated from aqueous alcohol in orange needles, m. p. 242° (decomp.) (Found: N, 11·7. $C_{25}H_{28}O_7N_4$ requires N, 11·3%). The *di*-O-*methyl ether* was prepared by the methyl sulphate–potassium carbonate method, purified by chromatography on aluminium oxide from benzene, and crystallised from methanol, forming yellow prisms (0·5 g.), m. p. 55° [Found: C, 73·2; H, 8·3; OMe, 18·5. $C_{19}H_{22}O_2(OMe)_2$ requires C, 73·2; H, 8·2; OMe, 18·0%]. This ether was readily soluble in the usual organic solvents, had a negative ferric reaction in alcohol, and gave a 2 : 4-*dinitrophenylhydrazone* which separated from ethyl acetate in red prisms, m. p. 211° (decomp.) [Found: N, 10·7; OMe, 11·8. $C_{25}H_{26}O_5N_4(OMe)_2$ requires N, 10·7; OMe, 11·8%].

Tetrahydrosclerotoquinone (0·5 g.) with acetic anhydride (4 ml.) with a drop of sulphuric acid, sodium acetate (0·1 g.), or pyridine, on the steam-bath for ½ hr., gave the *diacetate*, which separated from methanol in yellow needles (0·4 g.), m. p. 94°, $[\alpha]_D^{22}$ +8·3° (*c* 2·19 in EtOH), $\lambda_{max.}$ 258, 274, 340 mμ (log ε 4·45, 4·20, 3·54 respectively) (Found: C, 68·9, 69·0; H, 7·0, 7·2. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·1%). Reductive acetylation of the quinone (0·5 g.) with acetic anhydride (8 ml.), zinc dust (0·5 g.), and sodium acetate (0·5 g.) on the steam-bath for 15 min. gave *tetra*-O-*acetyltetrahydrosclerotoquinol* which separated from methanol in needles (0·4 g.), m. p. 88°, $\lambda_{max.}$ 234, 289, 336 mμ (log ε 4·94, 3·79, 1·90 respectively) [Found: C, 66·6; H, 7·0; CH_3·CO, 35·1. $C_{19}H_{22}(OAc)_4$ requires C, 66·7; H, 7·0; CH_3·CO, 35·4%].

Oxidation of Tetrahydrodi-O-methylsclerotoquinone.—A solution of potassium permanganate (3 g.) in water (80 ml.) was added gradually in 2 hr. to the di-*O*-methyl ether (0·5 g.), in acetone (50 ml.), and 24 hr. later the mixture was clarified with sulphur dioxide, concentrated in a vacuum to 50 ml., and extracted with ether (3 × 25 ml.). The combined ethereal extracts were washed with 2N-aqueous sodium hydrogen carbonate (4 × 20 ml.), and the washings acidified. Extraction of this with ether gave a *phthalic acid* which separated from benzene–light petroleum (b. p. 60—80°) in needles (0·15 g.), m. p. 72° [Found: C, 62·4; H, 8·0; OMe, 9·7. $C_{16}H_{21}O_4(OMe),H_2O$ requires C, 62·6; H, 8·0; OMe, 9·5%]. This acid, which is readily soluble in the usual organic solvents except in light petroleum, gave an intense fluorescein reaction. Distilled at 110°/0·01 mm., the acid (1 g.) furnished the *anhydride* (0·8 g.), m. p. 44°, $[\alpha]_D^{20}$ +16·3° (*c* 1·36 in EtOH), $[M]_D^{20}$ +4727° (Found: C, 69·6; H, 7·9; OMe, 11·2%; *M*, 295. $C_{16}H_{19}O_3$·OMe requires C, 70·3; H, 7·6; OMe, 10·7%; *M*, 290). Interaction of the anhydride (0·12 g.) with aniline (0·2 g.) in benzene (4 ml.) on the steam-bath for 5 min. yielded the *anilic acid* which separated from light petroleum (b. p. 60—80°) in needles (0·15 g.), m. p. 157° (Found: C, 72·2; H, 7·7; OMe, 8·1; N, 3·7. $C_{22}H_{26}O_3N$·OMe requires C, 72·0; H, 7·6; OMe, 8·1; N, 3·7%). Similarly prepared, the m-*toluidic acid* crystallised from benzene–light petroleum (b. p. 60—80°) in needles (0·2 g.), m. p. 148° (Found: C, 72·1; H, 7·8; N, 3·4. $C_{24}H_{31}O_4N$ requires C, 72·5; H, 7·9; N, 3·5%). The β-*naphthylamic acid* formed needles, m. p. 173°, from benzene (Found: C, 74·6; H, 7·4; N, 3·4; OMe, 7·0. $C_{26}H_{28}O_3N$·OMe requires C, 74·8; H, 7·2; N, 3·2; OMe, 7·2%).

Boiling for ½ hr. with methanol (3 ml.), water (20 ml.), and sodium hydroxide (2 g.) converted the anhydride into the phthalic acid (0·3 g.), m. p. and mixed m. p. 72° after purification from benzene–light petroleum (b. p. 60—80°).

The phthalic acid (1 g.) in ether (30 ml.) with an excess of ethereal diazomethane furnished the *dimethyl ester* (0·75 g.), b. p. 120—125°/0·01 mm. [Found: C, 66·5; H, 7·5; OMe, 25·1. $C_{14}H_{19}(OMe)(CO_2Me)_2$ requires C, 67·8; H, 8·4; OMe, 27·6%]. Treatment of this ester (0·5 g.) in ether (30 ml.) with ammonia at 0° gave an oil, which did not crystallise but on alkaline hydrolysis gave the phthalic acid (0·3 g.), m. p. and mixed m. p. 72°, and ammonia.

A mixture of the phthalic acid (0·2 g.), hydriodic acid (3 ml.; *d* 1·7), and acetic acid (from 2 ml. of anhydride) was heated under reflux for ½ hr., cooled, diluted with water (30 ml.), and extracted with ether (3 × 25 ml.). Evaporation of the washed, dried ethereal extracts furnished a pale yellow oil, with a negative ferric reaction and devoid of methoxyl groups, which readily dissolved in 2N-aqueous sodium hydrogen carbonate and gave an intense fluorescein reaction.

Degradation of Dihydrosclerotiorin with Alkali.—A mixture of dihydrosclerotiorin (2 g.), zinc dust (2 g.), and 5% aqueous potassium hydroxide (100 ml.) was heated under reflux in nitrogen for 5 min. and the resulting solution filtered, cooled, and added to an excess of 5N-hydrochloric acid. The pale brown precipitate was isolated with ether (5 × 50 ml.), and the solution washed successively with aqueous 2N-sodium hydrogen carbonate, 2N-sodium carbonate, and 2N-sodium hydroxide. On acidification of these extracts only the deep violet sodium carbonate solution furnished a precipitate, which was most readily purified by sublimation in a vacuum at 195°/0·005 mm. followed by crystallisation from alcohol, giving *dihydrosclerotoquinone* in bright orange needles (0·5 g.), m. p. 219—220° (decomp.), $\lambda_{max.}$ 271, 304 mμ (log ε 5·02, 4·14 respectively) (Found: C, 72·5; H, 6·7. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·0%). This quinone gives a violet solution in 2N-aqueous sodium carbonate and a red ferric reaction in alcohol. Methylation of the quinone (0·8 g.) by methyl sulphate–potassium carbonate for 2½ hr. furnished the *di*-O-*methyl ether* which separated from methanol in long yellow needles (0·7 g.), m. p. 98°, which changed to stout yellow prisms, m. p. 98°, on prolonged contact with the solvent [Found: C, 73·8; H, 8·0; OMe, 17·8. $C_{19}H_{20}O_2(OMe)_2$ requires C, 73·7; H, 7·7; OMe, 18·1%]. The ether had a negative ferric reaction in alcohol. On acetylation by pyridine–acetic anhydride dihydrosclerotoquinone (0·2 g.) gave the *di*-O-*acetate* in yellow plates (0·15 g.), m. p. 116°, with a negative ferric reaction (Found: C, 69·2; H, 6·4. $C_{23}H_{26}O_6$ requires C, 69·3; H, 6·6%).

Reductive acetylation of dihydrosclerotoquinone (0·8 g.) with sodium acetate (1 g.) and zinc dust (1 g.) in boiling acetic anhydride (5 ml.) for ½ hr. gave *tetra*-O-*acetyldihydrosclerotoquinol* in needles or prisms (0·65 g.), m. p. 139° (from methanol), $\lambda_{max.}$ 234, 280, and 289 mμ (log ε 4·91, 3·70, and 3·71 respectively) (Found: C, 67·1; H, 7·0. $C_{27}H_{32}O_8$ requires C, 66·9; H, 6·7%). A stream of ozone and oxygen was passed into a solution of this tetra-acetate (0·5 g.) in ethyl acetate (50 ml.) at room temperature for 20 min., the solvent was removed *in vacuo*, and the

colourless residue treated with water (50 ml.). Next day a solution of the amorphous solid (0·2 g.) in methanol (10 ml.) was mixed with 2N-aqueous potassium hydroxide (5 ml.) and 5 min. later the violet solution was poured into 2N-hydrochloric acid (50 ml.), the precipitate was extracted with ether, and the extract was washed with 2N-aqueous sodium hydrogen carbonate. Obtained by the acidification of this violet alkaline solution, the solid was purified by sublimation at 210°/0·01 mm. to yield a mixture of pale yellow and orange products which were separated by fractional crystallisation from methanol, giving (*a*) a *furanonaphtha*-p-*quinone* in orange needles (20 mg.), m. p. 234°, sparingly soluble in methanol and insoluble in 2N-aqueous sodium hydrogen carbonate (Found: C, 69·3, 68·9; H, 4·5, 4·7. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·2%), and (*b*) an *acetonylhydroxynaphtha*-p-*quinone* in yellow needles (15 mg.), m. p. 225°, readily soluble in methanol and in 2N-aqueous sodium hydrogen carbonate to an intense violet solution (Found: C, 64·7, 64·5; H, 4·3, 4·0. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%). The furanonaphthaquinone was unchanged by sublimation at 220°/0·01 mm. but the acetonylhydroxynaphthaquinone gave a mixture of unchanged compound and the furanonaphthaquinone. The mixed m. p. of the two quinones was *ca.* 207°.

Degradation of ***Pentanordihydrosclerotiorone*** (XX) *with Alkali.*—(*a*) A mixture of this compound [1] (1 g.), zinc dust (1 g.), and 5% aqueous potassium hydroxide (100 ml.) was heated under reflux in nitrogen for 5 min., cooled, mixed with an excess of 2N-hydrochloric acid, and extracted with ether. The ethereal solution was washed with 2N-aqueous sodium hydrogen carbonate and the violet extract acidified, giving a solid which on sublimation in a vacuum furnished two products; (i) at 180°/0·01 mm., a colourless solid which on purification from methanol furnished a *phenol* (150 mg.) in needles, m. p. 224°, with an intense red-brown ferric reaction in alcohol and readily soluble in 2N-aqueous sodium hydrogen carbonate [Found: C, 60·2, 59·8; H, 4·9, 4·8; Cl, 13·5, 13·2, 13·0%; *M* (Menzies–Wright in C_6H_6), 279. $C_{14}H_{13}O_4Cl$ requires C, 60·0; H, 4·6; Cl, 12·7%; *M*, 280·5]; and (ii) at 210°/0·01 mm., a mixture of the two naphtha-*p*-quinones which was resolved as described previously into the furanonaphtha-*p*-quinone (10 mg.), m. p. and mixed m. p. 234°, and identical infrared spectra, and the acetonylhydroxynaphthaquinone (5 mg.), m. p. and mixed m. p. 225°, and identical infrared spectra.

(*b*) Compound (XX) (1 g.) was added to a mixture of 5% aqueous potassium hydroxide (50 ml.) and zinc dust (1 g.) at −3°, in nitrogen, and 15 min. later the filtered solution was added to an excess of 2N-hydrochloric acid. From an ethereal solution of the precipitate 2N-aqueous sodium hydrogen carbonate extracted a pale brown solid which was purified by repeated crystallisation from methanol, giving the phenol, m. p. and mixed m. p. 224°; this was more conveniently purified by sublimation at 180°/0·01 mm. followed by crystallisation from alcohol; the yield was 0·2 g. Under these conditions quinonoid substances were not formed. Heated under reflux with zinc dust (0·5 g.) and 5% aqueous potassium hydroxide (50 ml.) for 10 min., this phenol (0·2 g.) was recovered unchanged on acidification of the cooled solution (yield of compound, 0·1 g., m. p. and mixed m. p. 224°). The phenol furnishes iodoform under standard conditions.

The ultraviolet absorption spectra were determined in 95% alcohol with a Unicam S.P. 500 Spectrophotometer and the infrared spectral data were obtained in Nujol on a Grubb-Parsons double-beam spectrophotometer. The analyses were by Mr. A. S. Inglis, M.Sc. and his associates of this Department.

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